

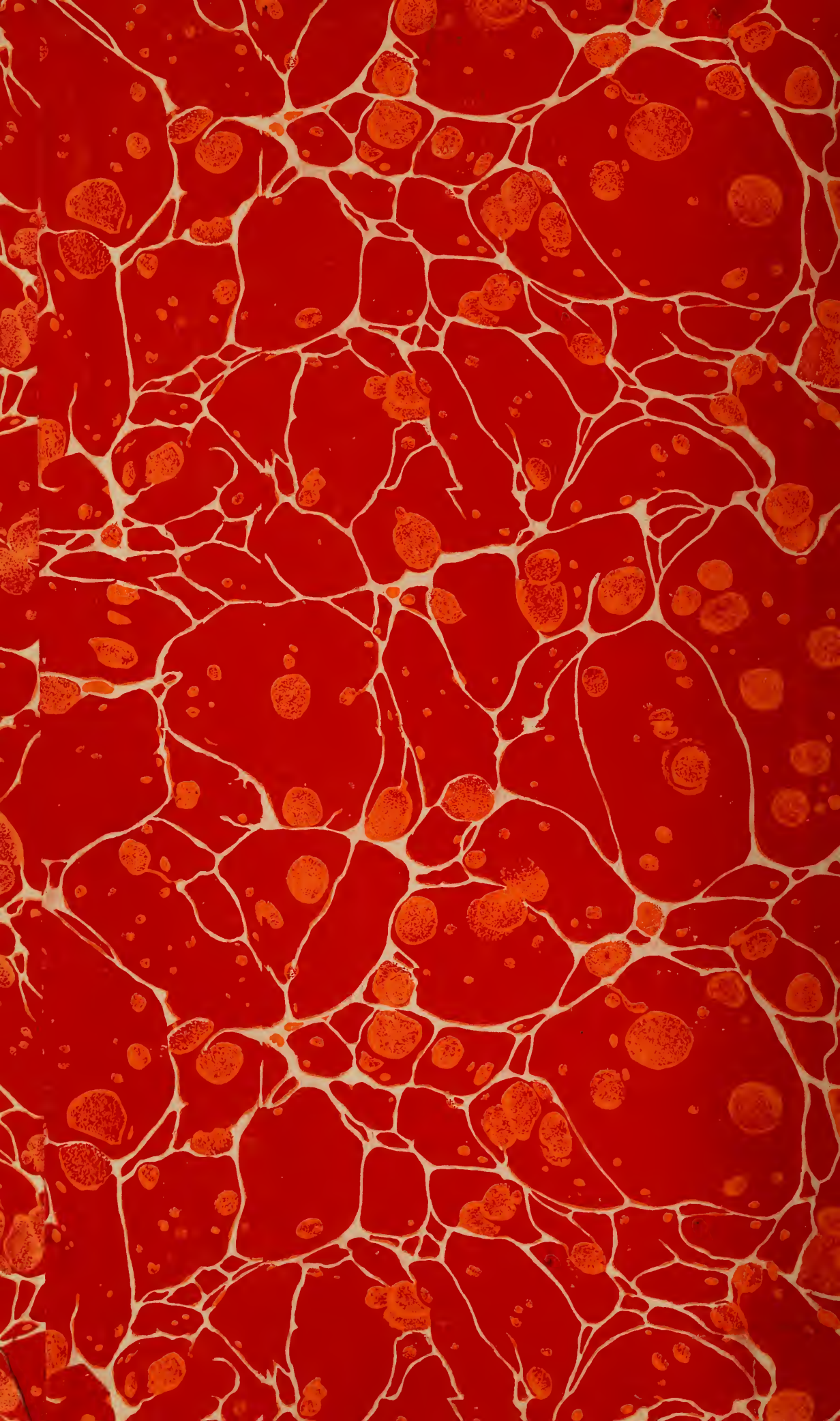
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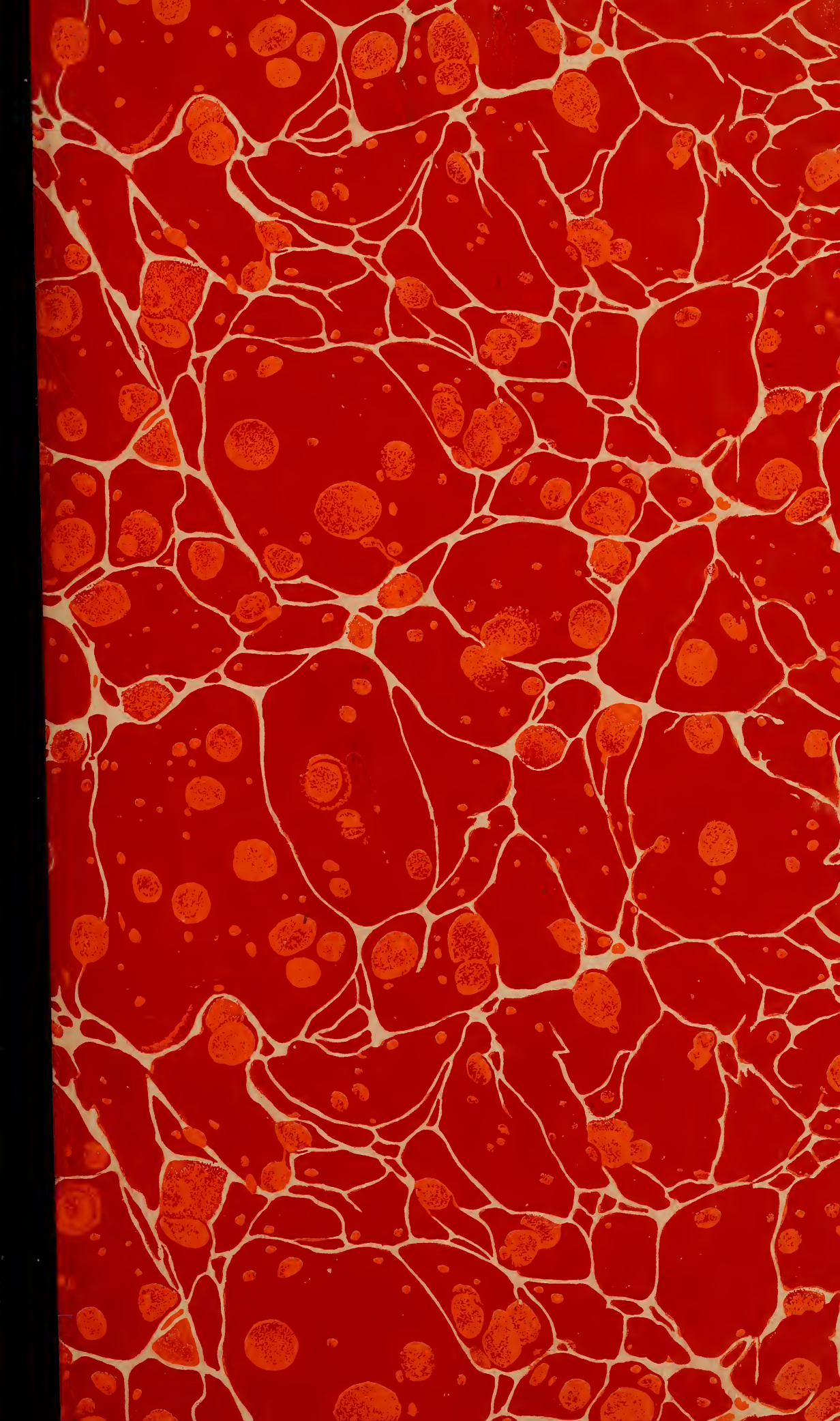
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ISOLATION OF NORMAL NONANE FROM A MIDCONTINENT PETROLEUM¹

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ABSTRACT

An account is given of the separation of *n*-nonane in a high state of purity from a midcontinent petroleum by alternating fractional distillation and fractional crystallization. The density, refractive index, boiling point, freezing point, and infra-red absorption spectrum of the product are given and compared with the same properties of synthetic *n*-nonane. It is concluded that the petroleum under investigation contains about 1 per cent of *n*-nonane by weight.

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I. INTRODUCTION

The presence of *n*-nonane in American petroleum has been reported by several investigators.³ The evidence given for its isolation is, however, not conclusive, except for the sample of very pure nonane obtained by Shepard, Henne, and Midgley with the aid of the chlorosulfonic acid process. The present paper describes the isolation of *n*-nonane from an Oklahoma petroleum.⁴ Separation of this hydrocarbon in a high state of purity was accomplished by alternating fractional distillation and fractional crystallization.

II. INITIAL DISTILLATION

Approximately 600 gallons (2,300 liters) of the crude petroleum, which had been fractionated in a semicommercial still into 20-liter cuts,⁵ was distilled thrice through a 20-plate bubbling-cap column of steel⁶ in an atmosphere of carbon dioxide. The distillate collected at the rate of 500 ml an hour and was separated into cuts each having

¹ This paper describes some of the results obtained in an investigation on the separation, identification, and determination of the chemical constituents of commercial petroleum fractions listed as project No. 6 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the central petroleum committee of the National Research Council.

² American Petroleum Institute research associate.

³ C. M. Warren, Proc. Am. Acad. Arts Sci., vol. 27, p. 80, 1891, communicated May 12, 1868; C. F. Mabery, Proc. Am. Acad. Arts Sci., vol. 31, pp. 33, 57, 1895; G. G. Brown and A. R. Carr, Ind. Eng. Chem., vol. 18, p. 722, 1926; A. F. Shepard and A. L. Henne, Ind. Eng. Chem., vol. 22, p. 356, 1930; A. F. Shepard, A. L. Henne, and T. Midgley, jr., J. Am. Chem. Soc., vol. 53, p. 1948, 1931.

⁴ For further description and properties see E. W. Washburn, B. S. Jour. Research, vol. 2, p. 469, 1929.

⁵ See J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 607, 1931.

⁶ J. H. Bruun and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 470, 1929.

a 2° to 3° boiling range. Under the direction of S. T. Schick Tanz,⁷ the fractions boiling within the range 130° to 160° C. and having a total volume of approximately 175 liters were subjected to further fractionation in the 30-plate glass stills described in another publication.⁸ The material was distilled with a reflux ratio of about 10:1 and the distillate was collected at the rate of 1 ml per minute in 1° cuts. A slow stream of dry carbon dioxide was bubbled continuously into the still pot throughout the distillation to minimize cracking and to prevent oxidation.

III. FRACTIONAL CRYSTALLIZATION

The initial freezing points of a certain few of the distillation fractions shown in Figure 1 are displayed in Figure 2. These fractions were subjected to a systematic fractional crystallization by a process



FIGURE 1.—Distribution of volume of the fractions over the boiling range after two distillations through the glass stills

of equilibrium melting previously described.⁹ Cuts were made in accordance with the refractive index and those for which $n_D^{20} > 1.416$ were subjected to further distillation. Systematic fractionation, made in this manner by alternating crystallization and distillation as required, yielded finally about 18 liters of material with a refractive index of $n_D^{20} = 1.416$ or less, which after further crystallization gave about 10 liters of nonane, $n_D^{20} = 1.407$, as compared with 1.405, which is the value given for *n*-nonane in International Critical Tables.¹⁰

This approximately pure material was then distilled through a 35-foot column packed with jack chain,¹¹ under a pressure of 215 mm.

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⁸ J. H. Bruun and S. T. Schick Tanz, *B. S. Jour. Research*, vol. 7, p. 851, 1931.

⁹ R. T. Leslie and S. T. Schick Tanz, *B. S. Jour. Research*, vol. 6, p. 331, 1931.

¹⁰ *Int. Crit. Tables*, I, p. 230, 276, McGraw Hill Book Co., 8 1926.

¹¹ See footnote 8.

A large reflux ratio was maintained and the distillate collected at the rate of 1 ml per minute. The first 10 per cent distilled within 0.3°C . of the boiling point of *n*-nonane and possessed a refractive index from one to two units in the third decimal place higher than that of pure nonane. The remainder distilled (within a tenth of a degree) at exactly the temperature at which *n*-nonane possesses a vapor pressure of 215 mm. The refractive index of the distillate agreed, to one unit in the third decimal place, with that of pure nonane. The residue in the still pot, comprising about 10 per cent of the original charge, had a higher refractive index than that of *n*-nonane but slightly less than that of the first 10 per cent distilled.

From this distillation about 9 liters of nearly pure *n*-nonane were obtained in five lots, listed in Table 1 as Lots I to V. These lots represent the major portion of *n*-nonane obtained in the present investigation.

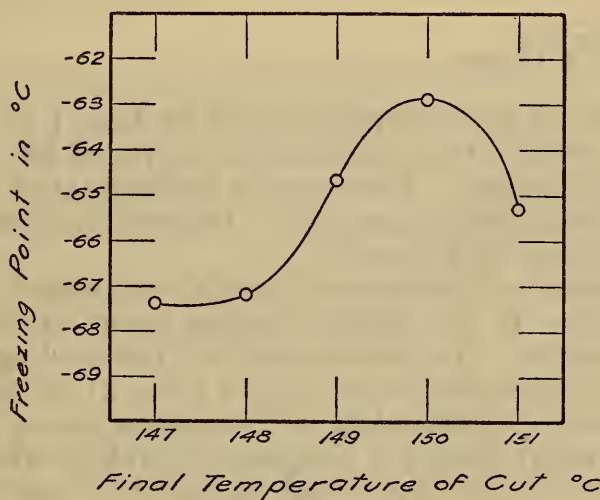


FIGURE 2.—Variation in initial freezing point of the fractions with the boiling range

IV. PROPERTIES OF THE FINAL PRODUCT

In Table 1 the physical properties of the product are compared with those of synthetic *n*-nonane,¹² and with those given by Shepard, Henne, and Midgley¹³ for *n*-nonane isolated from petroleum. Densities were determined by E. E. Hill, of the weights and measures division, and refractive indices were measured by L. W. Tilton, of the optics division of this bureau.

Boiling points were determined in a modified McCoy boiling-point apparatus. In each case the thermometer was supported above the liquid in the inner tube. Unless otherwise specified, a 25-ohm platinum resistance thermometer was used.

¹² Prepared in this bureau by B. J. Mair.

¹³ See footnote 3, p. 907.

TABLE 1.—Comparison of the properties of *n*-nonane obtained from petroleum with the properties of synthetic *n*-nonane

Material	Volume	d_D^{20} ±0.00003	n_D^{20} ±0.0001	Boiling point 760 mm Hg	Initial freezing point	Mole per cent <i>n</i> - nonane
	<i>ml</i>			°C.	°C.	
Lot I.....	2,000	-----	1.4041	^a 150.5	^b -54.4	95.8
Lot II.....	2,000	-----	1.4042	^a 150.6	^b -54.5	95.4
Lot III.....	2,000	-----	1.4042	^a 150.6	^b -54.5	95.4
Lot IV.....	2,000	-----	1.4043	^a 150.6	^b -54.6	94.9
Lot V.....	600	-----	1.4035	^a 150.7	^b -53.9	98.7
Best sample (by physical means).....	75	0.71793	1.4033 _s	^c 150.73 ±0.01	^c -53.65	99.9
Best sample (by chlorosulfonic acid).....	73	.71803	1.4034 _s	^c 150.72 ±0.01	^c -53.76	99.2
Shepard, Henne, and Midgley.....	-----	.71780	1.4034 _o	150.71 ±0.01	-53.68	-----
Synthetic <i>n</i> -nonane.....	-----	.71770	1.4033 _s	^c 150.72 ±0.01	^c -53.70	-----

^a Relative boiling points only.^b Relative freezing points only.^c Values determined by B. J. Mair.

In addition to the product represented by Lots I to V in Table 1, a small sample of very pure nonane was prepared by continuing the fractional crystallization. This sample is designated in Table 1 as "best sample (by physical means)." Its purity is indicated by its freezing curve—curve I, Figure 3.

The mole percentage of *n*-nonane in each lot obtained was calculated from the difference in the initial freezing point of the sample and that of pure nonane. An examination of the cooling curve of the best sample of the isolated nonane (curve I, fig. 3) at the point where crystallization was approximately half complete shows that the traces of impurities present caused a temperature fall of about 0.015° C.; from which it follows that the initial temperature was too low by the same amount.¹⁴ With this correction the freezing point of pure *n*-nonane becomes -53.63° C. This value was used for the purpose of calculating the purity of the different lots. For the heat of fusion of *n*-nonane the value calculated by Parks and Todd¹⁵ was used.

One other portion from Lots I to V was treated with chlorosulfonic acid. It has been shown¹⁶ that this acid readily attacks all side-chain hydrocarbons as well as aromatic and unsaturated ones, but only slowly attacks normal and unsubstituted naphthenic hydrocarbons. A mixture of 500 ml of Lot I and 200 ml of the acid was stirred constantly for 18 hours, after which the acid layer was removed, a fresh portion of acid added, and the treatment continued for another 18 hours. At the end of this time all action had apparently ceased. After separating the oil and acid layers the oil was washed with water to free it from acid and then with two separate portions of dilute potassium hydroxide. It was then washed again, dried over "Dehydrite," and fractionally distilled through the tall jack-chain column mentioned above.¹⁷ The properties of the middle 75 ml fraction of the 428 ml distilled are recorded in Table 1

¹⁴ W. P. White, J. Phys. Chem., vol. 24, p. 393, 1920.¹⁵ G. S. Parks and S. S. Todd, Ind. Eng. Chem., vol. 21, p. 1235, 1929.¹⁶ See footnote 3, p. 907; Shepard and Henne.¹⁷ In the particular instance at hand, fractional distillation would not be effective in separating *n*-nonane from a small amount of cyclooctane, if the latter were present, since the boiling points of the two compounds are almost identical. Upon distilling, however, all high-boiling material formed by the chlorosulfonic acid would be retained in the still pot.

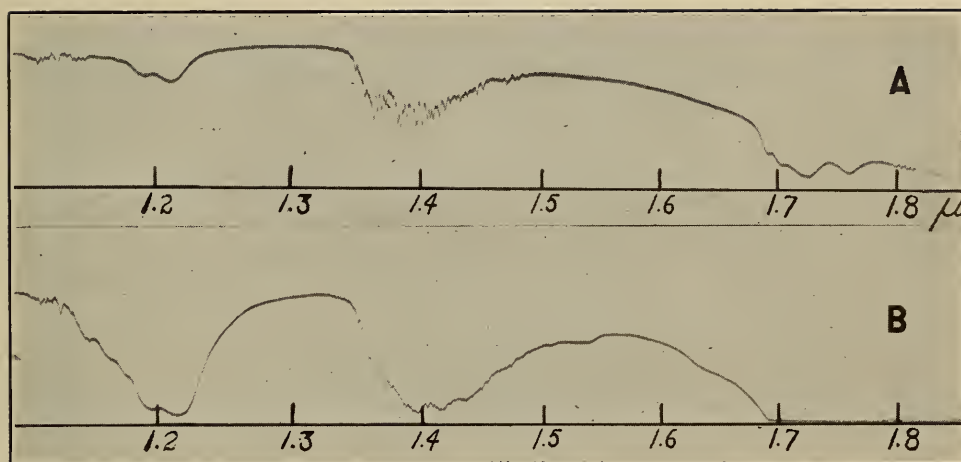


FIGURE 4.—*Infra-red absorption spectra of n-nonane*

Curves A and B are the automatically recorded energy transmission curves of the emission from a tungsten filament lamp through 1 mm and 1 cm cells, respectively, of normal nonane. The bands at $1.72\ \mu$ and $1.20\ \mu$ are the second and third harmonics, respectively, of the fundamental band at $3.43\ \mu$ which is observed in the absorption spectra of all hydrocarbons and is attributed to the H to C vibration. Absorption in the region of $1.4\ \mu$ is due to the combination frequency of the fundamentals at $3.43\ \mu$ and $6.86\ \mu$. The curves show a resolving power of about 10 Å to the slit width.



as those of "best sample (by chlorosulfonic acid)." The freezing curve for this sample is shown as Curve III in Figure 3.

Figure 4 shows the infra-red absorption spectra of the isolated nonane. The curves illustrated were obtained by U. Liddel, of the Fixed Nitrogen Laboratory, United States Department of Agriculture.

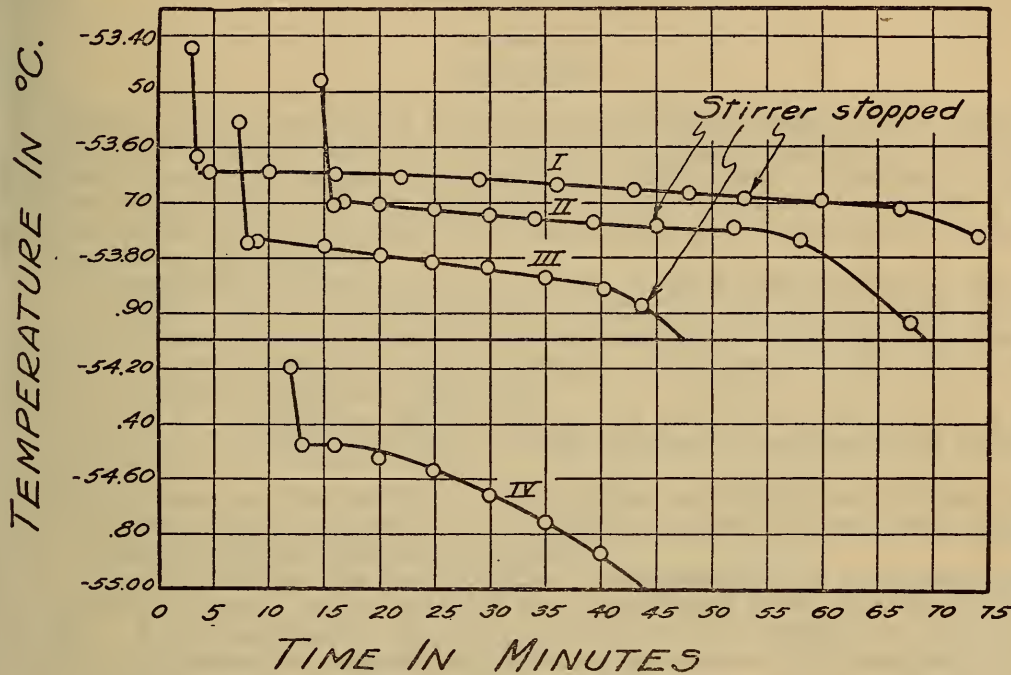


FIGURE 3.—Freezing curves of *n*-nonane

Curve I, best sample (by physical means).
II, synthetic *n*-nonane (Mair).
III, best sample (by chlorosulphonic acid).
IV, Lot II, main stock.

V. CONTENT OF *n*-NONANE IN THE CRUDE OIL

When allowance is made for losses which occurred in the various stages of the work, it is estimated that the crude petroleum used in this investigation contains about 1 per cent of *n*-nonane by weight.

VI. ACKNOWLEDGMENT

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WASHINGTON, August 17, 1931.

